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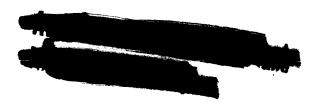
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ENHANCED OXIDATION OF PLATINUM IN ACTIVATED CARGES,

· IDENTIFICATION OF OXIDE FORMED

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ENHANCED OXIDATION OF PLATINUM IN ACTIVATED OXYGEN

III IDENTIFICATION OF OXIDE FORMED

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When platinum is oxidized above 800° C, a volatile oxide is formed that condenses on cold surfaces. The oxide formed in ordinary oxygen is PtO2.2 We have reported that PtO2 is also formed in activated oxygen; 3 the identification was made by means of electron diffraction from the condensed oxide film. In later work with activated oxygen we obtained several diffraction patterns similar to the one reported by Moore and Pauling⁵ for PtO; however, this pattern has been questioned by Galloni and Busch. 6 Proper identification of the oxide from diffraction patterns was complicated further by the diffuseness of the lines resulting from the poor crystalline structure of the oxide deposits, the dependence of the relative intensities of the lines on heat treatment, and the many similarities in the d values for Pt, Pt304, and Pt02. As a result a method of chemical analysis was developed to determine the stoichiometry of these oxide films. The method involved reduction of the oxide with hydrogen and determination of the resultant water by a microtechnique. The amount of platinum was determined by the usual colorimetric method using stannous chloride. 3,8

The oxide films were made in the apparatus described in reference 3, except that a microwave power supply was used to excite the discharge in the oxygen. During formation, the temperature of the platinum was maintained around 900° C. At this temperature, under the conditions of the

experiments, about 95% of the oxide formed resulted from the reaction of the 0 atom with the platinum. The remaining 5% arose from the reaction of the 0_2 molecule with the platinum. Samples were collected on the inside of removable quartz cylinders, 25 mm i.d. and 10 cm long. After formation they were placed in a desiccator over P_2O_5 and were analyzed as soon as possible; about 5 minutes. Three samples were made in oxygen containing 0.2% water vapor (dried at -80°C). The last sample was made in oxygen containing 3% water vapor. The results are shown in the following table:

| Amount of H ₂ O, | Amount of Pt, | Atomic ratio, |
|-----------------------------|---------------|---------------|
| μg | μg | 0/Pt |
| 26.4 | 146 | 1.96 |
| 25.8 | 13 5 | 2.07 |
| 22.2 | 110 | 2.18 |
| 20. 6 | 1.0 5 | 2.12 |

The analytically determined quantities are presented in the first two columns. The atomic ratio 0/Pt, calculated therefrom, is given in the third column. For each sample the atomic ratio is two within the 95% confidence limits of the method, which are ±12.5%. This formation of PtO₂ by 0 atoms is in agreement with the fact that metals are usually oxidized to their highest valence state in activated oxygen; in fact, silver can be taken to the +2 oxidation state.

Subsequent analysis of the "Pt0 diffraction pattern" mentioned in reference 4 indicated that it was a composite of Pt0₂, Pt₃0₄ and Pt lines. We have observed³ that the oxide deposits recombine 0 atoms to some degree, and are thereby heated. In runs in which the 0 atom concentration was high, some decomposition of the surface of the deposit

might have occurred. The "PtO patterns" were obtained from oxide films formed under such conditions. Furthermore, we have made controlled decomposition studies of PtO₂ deposits in the temperature range 400° to 450° C under 0.5 torr of oxygen, and it was shown that sometimes the decomposition leads to platinum only; very occasionally to Pt₃O₄ only; but generally to both Pt₃O₄ and platinum. The results were not very reproducible. Galloni and Busch⁶ have observed a similar behavior. Consideration of these observations leads one to conclude that the "PtO pattern" probably resulted from the partial decomposition of the PtO₂ deposit.

REFERENCES

- 1. G. C. Fryburg and H. M. Petrus, J. Electrochem. Soc. 108, 496 (1961).
- 2. C. B. Alcock and G. W. Hooper, Proc. Roy. Soc. A254, 551 (1960).
- 3. G. C. Fryburg, J. Chem. Phys. 24, 175 (1956).
- 4. G. C. Fryburg and H. M. Petrus, J. Chem. Phys. 32, 622 (1960).
- 5. W. J. Moore and L. Pauling, J. Am. Chem. Soc. 63, 1392 (1941).
- 6. E. E. Galloni and R. H. Busch, J. Chem. Phys. 20, 198 (1952).
- 7. G. C. Fryburg and D. A. Otterson, Anal. Chem. 35, 586 (1963).
- 8. G. H. Ayres and A. S. Meyer, Anal. Chem. 23, 299 (1951).
- 9. D. G. H. Marsden and J. W. Linnett, Fifth (International) Combustion Symposium (Reinhold Publishing Co., New York, 1955) p. 685.